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Second Report on the  
Investigation of Remedial Measures for  
Combating Accelerated Oxidation Induced by  
Vanadium Contamination

Research and Development Report 040088 ✓  
NSM-013-120 B

4 September 1956

By

W. J. Greenert and L. G. Richards

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U. S. NAVAL ENGINEERING EXPERIMENT STATION

Annapolis, Maryland

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ABSTRACT

The oxidation characteristics of vanadium contaminated surfaces as affected by various treatments are described. It was found that coatings of the alkaline earth oxides substantially reduce the corrosion of 25-20 chromium-nickel steel. Treatments are described in sufficient detail to permit the development of procedures for applying the remedial substance to an actual boiler.

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Brown  
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or

ADMINISTRATIVE INFORMATION

This investigation was authorized by Bureau of Ships letter S51/1-1 (343) serial 343-96 of 21 February 1955.

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## REPORT OF INVESTIGATION

## INTRODUCTION

Fireside metal supports and similar parts are subject to a rapid and catastrophic deterioration when contaminated with vanadium oxides. Source of vanadium is residuum fuel derived from crudes of certain areas of the world. The seriousness of this problem is increasing steadily because of a continuing trend toward higher operating temperatures in fuel burning equipment. If remedial measures are not found, economies inherent in the utilization of fuels from various sources together with common bunkering may be curtailed. As a complete solution to this problem is not at hand, it would seem expedient to consider available means for extending the service life of equipment under prevailing contaminating conditions.

Findings from an initial survey of remedial surface treatments to combat accelerated oxidation of fireside surfaces were presented in reference (a). These treatments were aimed at reducing the corrosion of surfaces which had been contaminated under the combustion of vanadium-bearing fuel oil. Of the treatments studied, those relying on alkaline earth oxides proved most effective.

Additional findings in the investigation of remedial treatments including the long-term effectiveness of calcium oxide are presented in this report. The relative effectiveness of a number of other substances is also shown. Other results include the effect of surface treatments on the water solution and removal of vanadium-bearing slags and scales.

## METHOD OF TEST

The effectiveness of various surface treatments in reducing accelerated oxidation of contaminated 25-20 Cr-Ni steel was determined by the oxygen consumption test. A description of this test is contained in reference (a). Briefly, the test measures the volume of oxygen consumed by an oxidizing surface. The tests reported herein were conducted at 1600°F and, except where indicated as otherwise, had a duration of three hours.

## RESULTS OF TEST

### Effect of Certain Metallic Oxides on the Oxygen Consumption of Laboratory Contaminated Specimens

Various oxides were applied to specimens of 25-20 Cr-Ni steel. These specimens were precontaminated in a pseudo-ash consisting of 37%  $V_2O_5$ , 49%  $NaVO_3$ , and 14%  $Na_2SO_4$ . The specimens were contaminated by immersing them in the ash for two hours at 1600°F. This treatment developed a surface which, when subsequently tested, had a total oxygen consumption of approximately 100 cc/sq in for three hours. This level of consumption is equivalent to that found for the most severely service contaminated tube support plate tested to date.

Thick water slurries of the following metallic oxides were applied to precontaminated specimens. Two coats were brushed on to the surface and dried for five minutes at 1400°F. Only one oxide was applied to a particular specimen.

Cupric Oxide	Chromium Trioxide
Barium Monoxide	Manganese Dioxide
Cadmium Oxide	Nickelic Oxide
Titanium Dioxide	Cobaltic Oxide

The oxygen consumption of coated and uncoated specimens were determined. Results of these tests are tabulated in Table 1. The effectiveness of the various oxides in arresting accelerated oxidation is indicated in Figure 1. Included in this figure are data on the alkaline earth oxides previously reported on.

It is apparent that of the substances tested only cadmium oxide approaches the effectiveness of alkaline earth oxides in remedial action. Surprisingly, barium monoxide was not nearly as effective as the peroxide or hydroxide. Poorest showing was made by chromium trioxide which greatly intensified the corrosive action.

In order to more firmly establish the oxide application as a sound remedy, the long term effect of a calcium oxide coating was examined. Oxidation characteristics of coated and uncoated specimens were determined over a period of 165 hours. The remedy consisted only of the initial application of calcium oxide. The results are shown in Figure 2. It is apparent that this remedy is highly effective even for extended periods of time. A photograph of the specimens after test is shown in Figure 3. The protection afforded is striking as the untreated



Table 1  
Results of Oxygen Consumption Tests of Remedial Coatings  
Coatings Applied to Laboratory Contaminated Specimens

Remedial Coating	Total Oxygen Consumed Per Sq In - CC			% Red. of Accelerated Oxidation
	1 Hr	2 Hr	3 Hr	
None	44	94	135	-
Cadmium oxide slurry, CdO cp	8	16	26	81
Nickelic oxide slurry, Ni <sub>3</sub> O <sub>4</sub>	22	45	64	53
Barium oxide slurry, BaO purified	20	49	75	44
Cobaltic oxide slurry, Co <sub>2</sub> O <sub>3</sub>	26	60	86	36
Cupric oxide slurry, CuO	27	60	91	33
Manganese dioxide slurry, MnO <sub>2</sub>	45	85	122	10
Titanium dioxide, TiO <sub>2</sub>	46	93	139	-2
Chromium trioxide, CrO <sub>3</sub>	87	169	242	-79

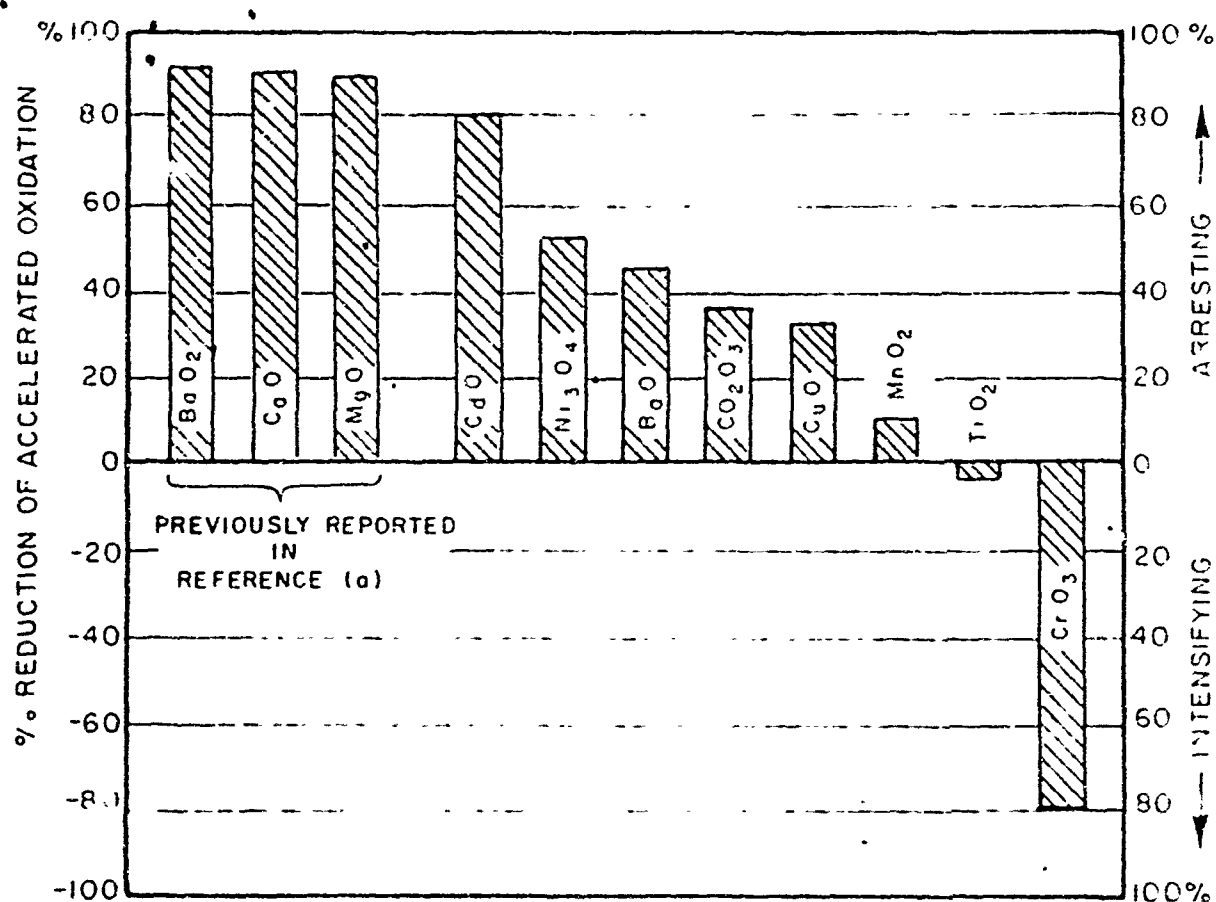


Figure 1  
Effectiveness of Remedial Substances in Arresting  
Accelerated Oxidation of Laboratory Contaminated Specimens

Test Temperature - 1600°F  
Specimen Material - 25-20 Cr-Ni Steel

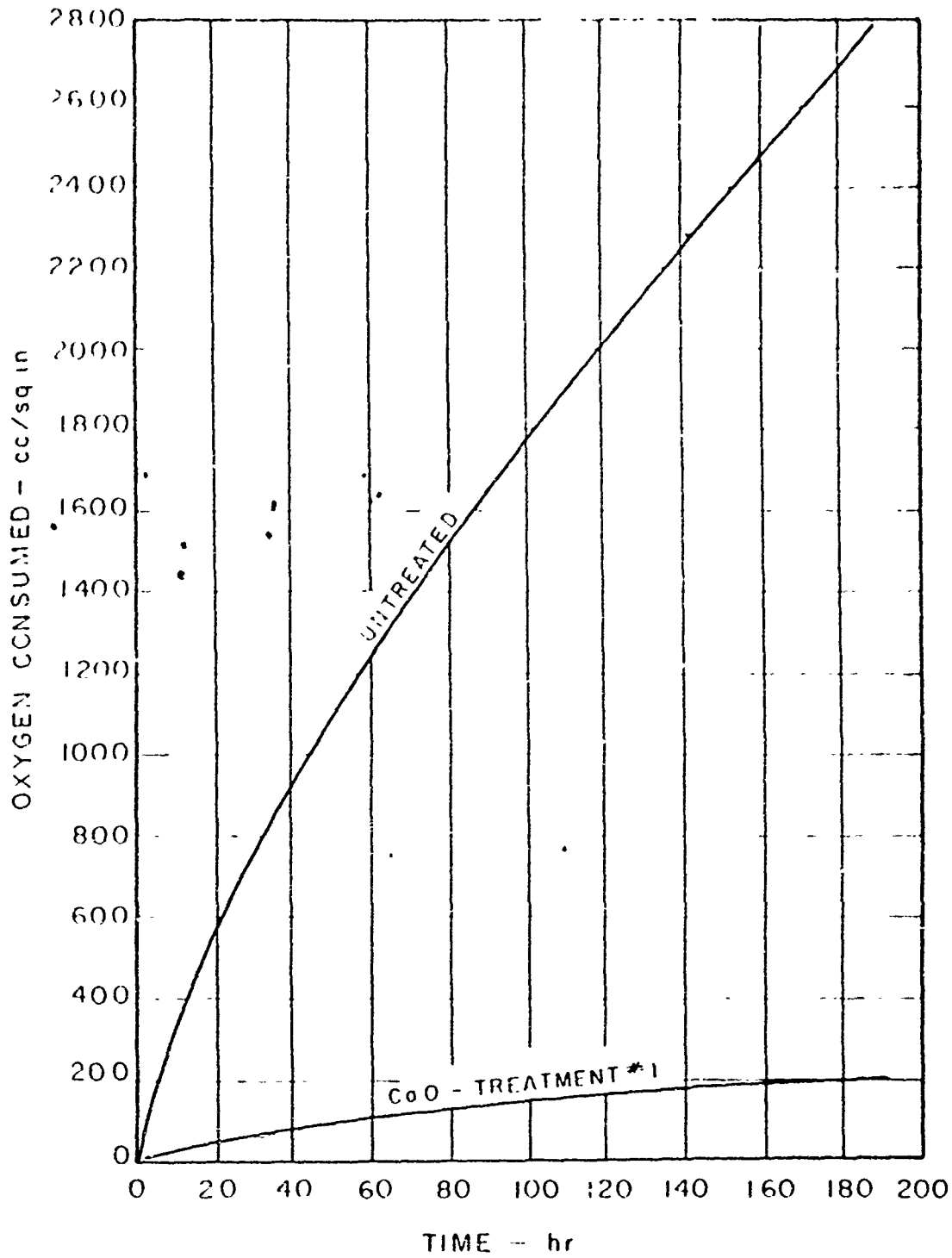
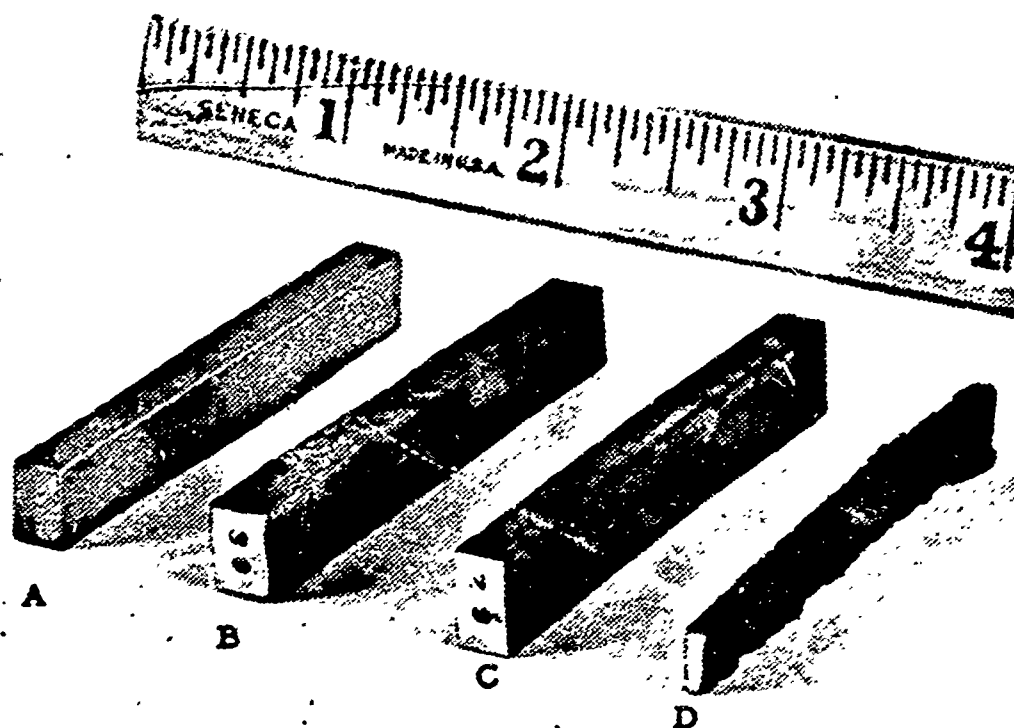


Figure 2  
Oxygen Consumption of Laboratory Contaminated Specimens  
Showing Effect of CaO Remedial Treatment During  
Long Term Oxidation Period

Specimen Material - 25-20 Cr-Ni Steel



- A = Contaminating scale removed - untested.
- B = Contaminating scale intact - untested.
- C = Remedied with CaO coating - tested 165 hours at 1600°F.
- D = Unremedied - tested 165 hours at 1600°F.

Figure 3

Accelerated Oxidation Test Specimens  
Showing Effect of CaO Remedy

specimen was largely consumed, whereas the coated specimen showed comparatively little damage. Of particular interest, is the persistent high rate corrosion of the uncoated specimen. As no replenishment of surface contaminant was made, the accelerant appears to be neither consumed or diluted during oxidation.

#### Effect of Certain Metallic Oxides on the Water Solubility of Slags

The effect of alkaline earth oxide applications on water solubilities of vanadium slags was studied. Pseudo slags consisting of  $V_2O_5$  with various proportions of  $CaO$ ,  $MgO$ , and  $BaO$  were prepared and their solubilities determined. A sample of service slag was treated with  $CaO$  and likewise tested.

Results of slag solubility tests are shown in Table 2. Additions of  $CaO$  and especially  $MgO$  to vanadium pentoxide greatly increased the water solubility of the resulting slag. On the other hand the additions of  $BaO$  has little effect. Apparently an optimum quantity for maximum solubility exists for both  $CaO$  and  $MgO$ . This appears to be between 8 to 20% for  $CaO$  and about 18% for  $MgO$ .

Included in Table 2 is the service slag from the USS CARPELLOTTI. The solubility increase affected by  $CaO$  is not so pronounced. However, the slag itself contained 11% total of calcium and magnesium (see reference (d)). Thus, on heating to  $1600^\circ F$ , considerable solubility was induced by substances already in the slag.

The phase diagram of the  $V_2O_5 - CaO$  system, as depicted by Morosov in reference (b), is presented in Figure 4. Calcium vanadates are shown at 23, 38, and 48%  $CaO$ . These correspond to mol ratios of 1:1, 1:2, and 1:3 of  $V_2O_5$   $CaO$ , respectively. A eutectic at 8%  $CaO$  is also shown. Mellor, in reference (c), states that various  $V_2O_5 \cdot CaO \cdot xH_2O$  compounds are water soluble. Deposits of these compounds are found in nature.

The results presented in Table 2 show that slags formed from 1:2 and 1:3 mixtures of  $V_2O_5$   $CaO$  and  $V_2O_5$   $MgO$  were much less water soluble than the 1:1 mixture slags. Also, the water solubility of the eutectic slag was quite low.

Table 2

## Solubility of Vanadium Slags in Water

Slag Constituents	Mol Ratio	Temp of Slag Formation °F	Observed Melting Point °F	% Soluble
V <sub>2</sub> O <sub>5</sub> cp		1600		4
V <sub>2</sub> O <sub>5</sub> + 8% CaO		1200	1150	9.5
V <sub>2</sub> O <sub>5</sub> + 8% CaO		1600	1150	12
V <sub>2</sub> O <sub>5</sub> + 20% CaO*		1600		48
V <sub>2</sub> O <sub>5</sub> + 23% CaO	1-1	1600		37
V <sub>2</sub> O <sub>5</sub> + 38% CaO	1-2	1900	1800	15
V <sub>2</sub> O <sub>5</sub> + 48% CaO	1-3	2300	2200	1
V <sub>2</sub> O <sub>5</sub> + 18% MgO	1-1	1600	1430	94
V <sub>2</sub> O <sub>5</sub> + 18% MgO	1-1	1600		88
V <sub>2</sub> O <sub>5</sub> + 33% MgO	1-2	2050	1950	61
V <sub>2</sub> O <sub>5</sub> + 43% MgO	1-3	2200	2050	21
V <sub>2</sub> O <sub>5</sub> + 20% BaO		1600	1050	10
V <sub>2</sub> O <sub>5</sub> + 46% BaO	1-1	1600	1375	2
Service slag from USS				
CARPELLOTTI, as removed		-		41
Same		1600		72
Same + 9.9% CaO	1-1*	1600		84

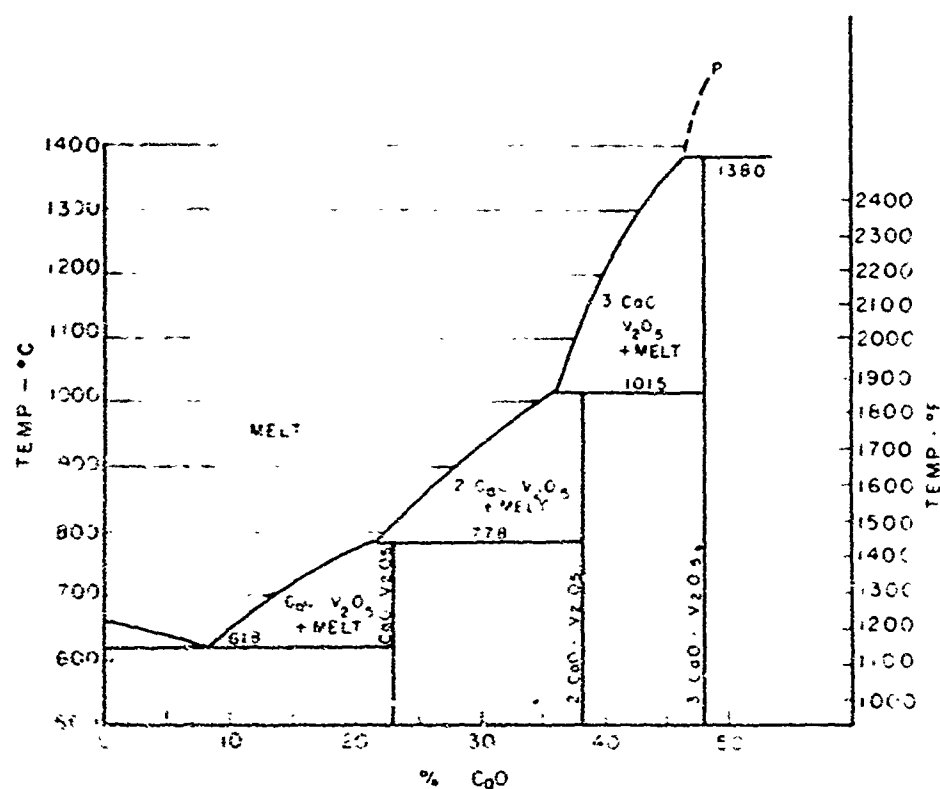
\* 1-1 mol ratio based on amount of equivalent V<sub>2</sub>O<sub>5</sub> in slag

Figure 4

Constitution Diagram of CaO-V<sub>2</sub>O<sub>5</sub> System  
From Reference (c)

### Effect of Water Washing on the Removal of Scale from Laboratory and Service Contaminated Specimens

The amount of scale removed in washing vanadium contaminated surfaces, represented by laboratory and service specimens, was investigated. The laboratory specimens were precontaminated as described earlier. The service specimens were removed from three failed superheater tube support plates. These plates exhibited vastly different surface conditions and probably represent variations in service operation. The plate from the USS CARPELLOTTI was heavily slagged and had a heavy, glazed black underlying scale. Very little metal wastage was apparent. The USS MALOY plate exhibited a tight, thin reddish scale over a smooth metal surface. No slag was present on the surface but considerable thinning of plate had occurred. The USS LEE plate exhibited a rough, porous, lumpy, brown scale over a roughly contoured metal surface. No slag was adhering to the surface and moderate thinning had occurred.

The above specimens, as-contaminated, annealed, and coated and annealed conditions, were given two 45-minute immersions in 190°F water. No mechanical cleaning action was done. The extent of scale removal was determined by weight loss and visual observation.

Results of the tests are shown in Table 3. The prewashing treatments promoted spalling and handling losses, which preclude weight loss comparison between the various specimens. Indications are, however, that MgO induces greater scale removal than does CaO. The effect of such treatments on accelerated oxidation of 25-20 Cr-Ni steel is shown in the next section.

### Effect of Remedial Treatments on the Oxygen Consumption of Laboratory and Service Contaminated Specimens

Oxidation characteristics of contaminated 25-20 Cr-Ni steel surfaces treated by various remedial methods were determined. Prior to remedial treatment, the laboratory specimens were contaminated with sulfur bearing or nonsulfur bearing pseudo-vanadium slags. The service specimens were as described in the preceding section. The following treatments were applied before the oxygen consumption test:

1. Treatment A - Water wash.
2. Treatment B - Anneal at 1600°F and water wash.

Table 3

Results of Water Washing Contaminated Surfaces  
(Specimens Immersed in 190°F Water)

Specimen	Remedy Treatment		Weight Loss on Water Wash gr./in. <sup>2</sup>	Observed Surface Change Due to Water Wash
	Coating	Treatment Prior to Washing		
Laboratory*	None	None	0.143	Some spalling at edges
	None	1600°F anneal	0.060	No change
	CaO	1600°F anneal	0.043	Smoothing of surface
	CaO	1600°F anneal	0.037	Smoothing of surface
	CaO	165 hr at 1600°F	0.163	Smoothing of surface
	MgO	1600°F anneal	0.177	Increased porosity, smoothing of surface
Tube support plate from USS CARPELLOTTI	None	None	0.040	Color change, gray to brown
	None	1600°F anneal	0.090	Increased porosity
	CaO	1600°F anneal	0.054	Scale removed from large areas
	MgO	1600°F anneal	0.046	Scale removed from large areas
Tube support plate from USS MALOY	None	None	0.002	Color change, red to black
	None	1600°F anneal	0.010	No change
	CaO	1600°F anneal	0.014	Smoothing of surface
	MgO	1600°F anneal	0.022	Increased porosity
Tube support plate from USS LEE	None	None	0.146	No apparent change
	None	1600°F anneal	0.072	Increased porosity - crumbly
	CaO	1600°F anneal	0.135	Smoothing of surface

\* 25-20 Cr-Ni steel pregasified in sulfur bearing vanadium slag

### 3. Treatment C - Calcium oxide coat.

4. Treatment D - Calcium oxide coat, anneal at 1600°F, and water wash.

Figures 5, to 9, inclusive, show oxidation curves for the above treatments and specimens. Examination of these curves reveals that Treatment D is generally more effective than Treatment C. Both treatments substantially reduce the corrosion from nonsulfated, high intensity, vanadium slags as well as from sulfated, low intensity, vanadium slags. The same treatments were also substantially effective when applied to the service contaminated surfaces.

## DISCUSSION

Details of the various remedial methods investigated are discussed in appropriate sections under Results of Tests.

Specimen Material - 25-20 Cr-Ni Steel  
 Slag - 37%  $V_2O_5$  - 49%  $NaVO_3$  - 14%  $Na_2SO_4$

Batch No. 1 - Slag ---  
 Batch No. 2 - Slag ———

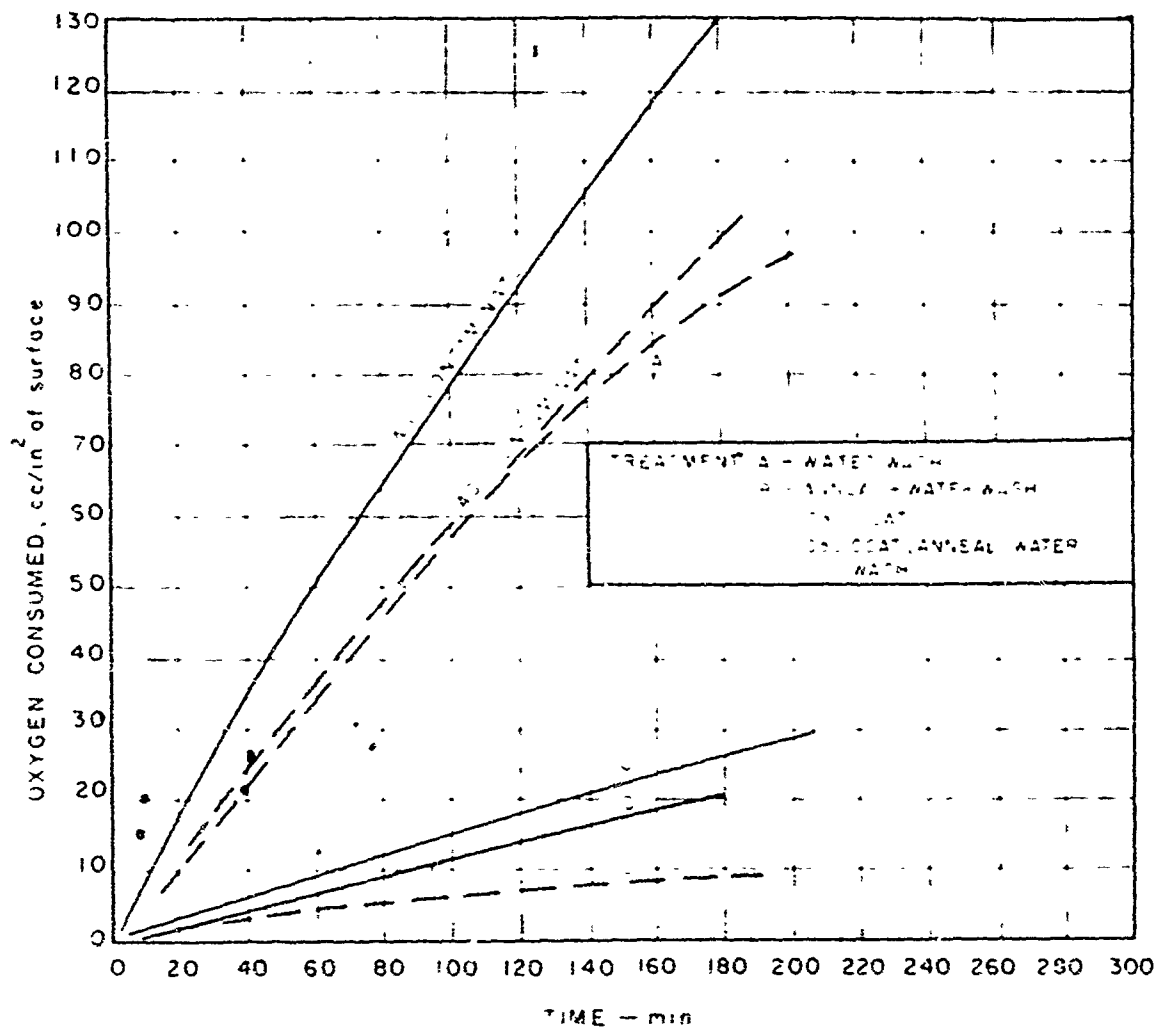
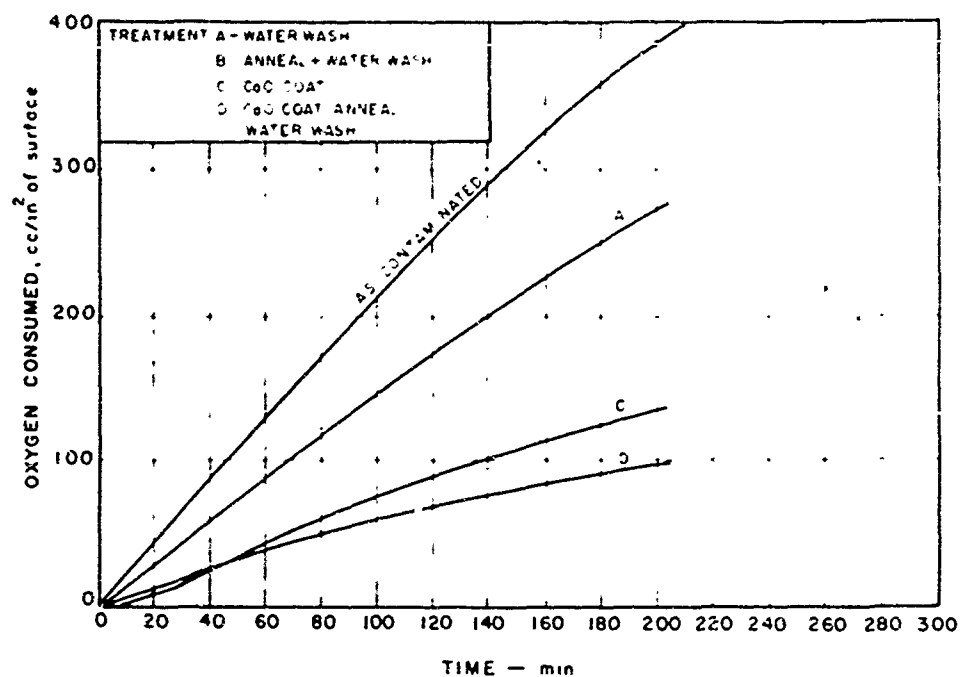


Figure 5

Effect of Remedial Treatments on  
 Surfaces Contaminated in Low Intensity Sulfated Slags





Specimen - 25-20 Cr-Ni Steel  
 Slag - 63% NaVO<sub>3</sub> - 37% V<sub>2</sub>O<sub>5</sub>

Figure 6  
 Effect of Remedial Treatments on  
 Surfaces Contaminated in High Intensity Nonsulfated Slag

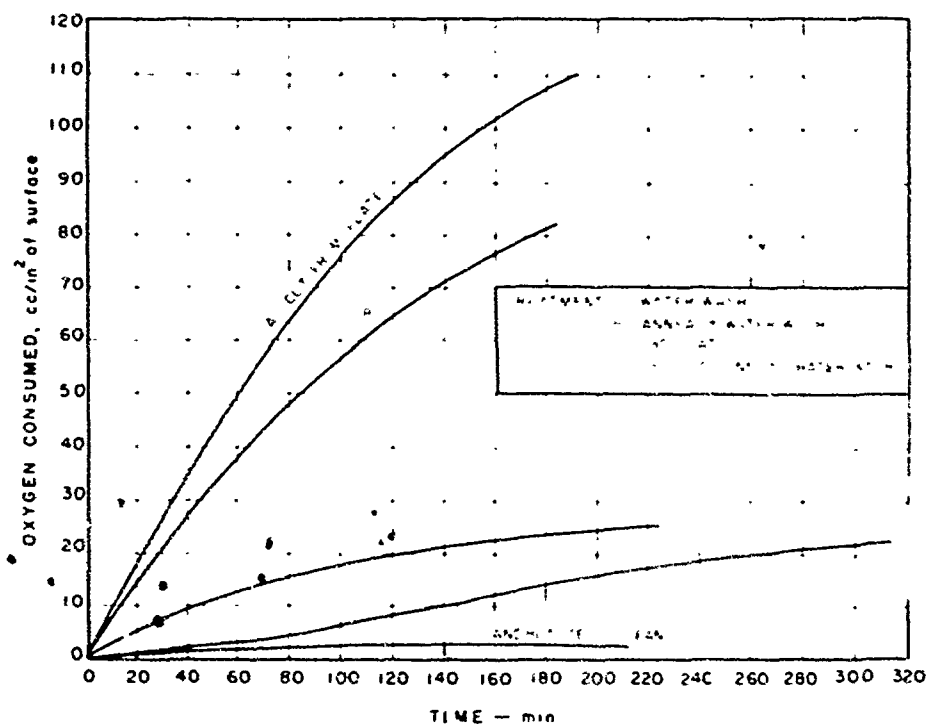


Figure 7  
 Effect of Remedial Treatments on USS CARPELLOTTI Tube Plate

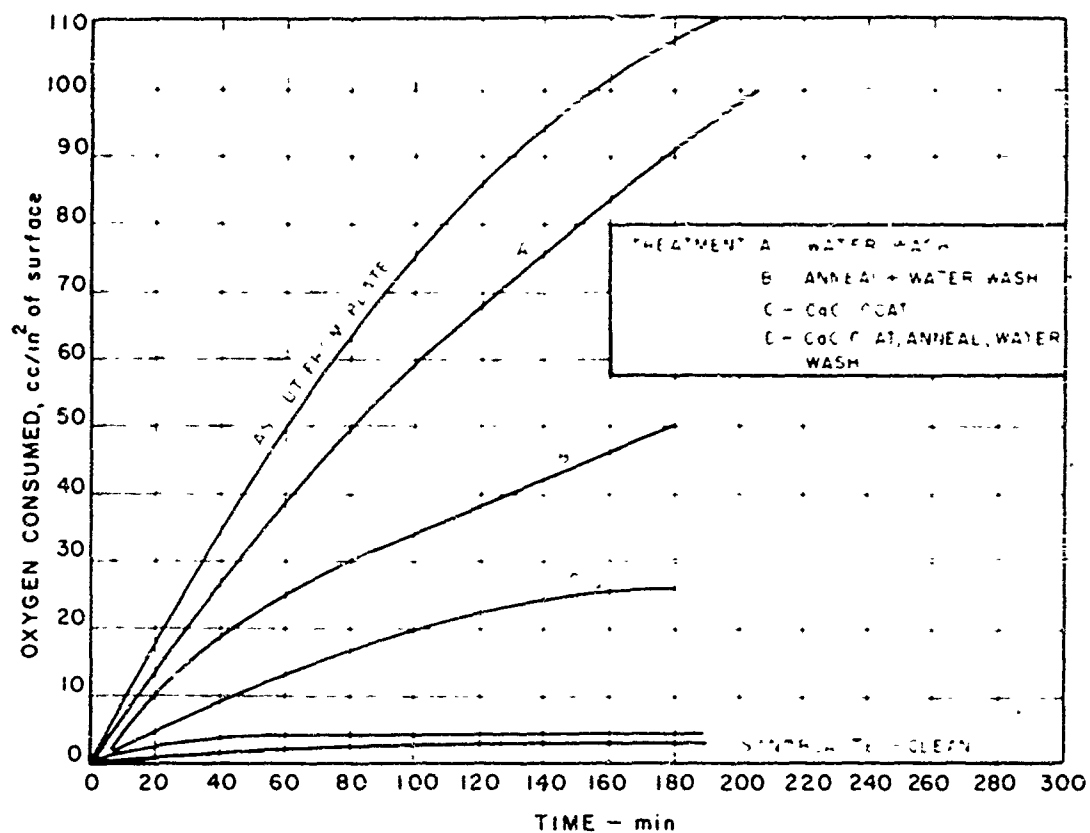


Figure 8  
Effect of Remedial Treatments on USS MALOY Tube Plate

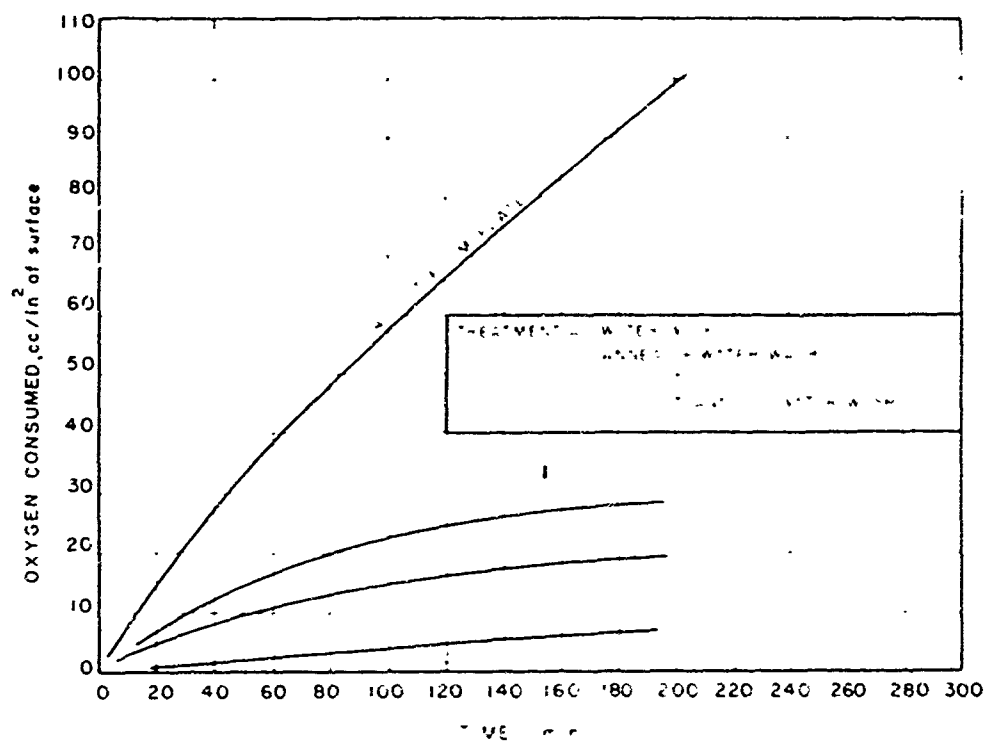


Figure 9  
Effect of Remedial Treatments on USS LEE Tube Plate

Results of these laboratory tests indicate that the accelerated oxidation of fireside surfaces induced by vanadium slags can be controlled by the application of certain substances to the contaminated surfaces. Substantial reductions in corrosion intensities of pseudo-slugs and service induced fireside scales occurred when alkaline earth oxides were applied. Calcium oxide and magnesium oxide not only inhibited corrosion but conditioned the slag and scale for easier removal. Of the two, calcium oxide performed more consistently in the tests. Also, test data presented in reference (a) showed that hydrated lime was as effective as chemically pure calcium oxide.

Suitable techniques for the application of these remedial substances to boilers in service would have to be developed. It would seem that this is a task for a boiler operating agency. The test data merely point out features that should be considered when setting up a procedure. Two treatments are visualized: one for use when the boiler is steaming or in stand-by status; the other for when the boiler is on down time as during repair or overhaul. The sensitive fireside surfaces should be coated periodically with an alkaline earth oxide or mixture of oxides. This assumes that a procedure for applying the coating during steaming and stand by can be worked out. The frequency of application and the amount of oxide required will be determined by the following factors. (a) vanadium content of fuel ash, (b) amount of fuel fired, and (c) visual observation of slag deposition. For example, firing an oil high in equivalent  $V_2O_5$  which exhibits a high deposition rate, would require more frequent and heavier application than for an oil low in  $V_2O_5$  with an equal deposition rate, or one high in  $V_2O_5$  with a low deposition rate. In reference (e) it was shown that the amount of  $V_2O_5$  occurring in fireside deposits is about 40% of that found by oil ash analysis. Calcium oxide in an amount equal to 23% of equivalent  $V_2O_5$  in the fireside deposit is needed for stoichiometric balance.

These vanadium bearing slags when coated with calcium or magnesium oxides and heated for a time form water soluble compounds. These compounds are formed within the temperature range 1150° to 1450°F. Tests have indicated that two hours at this temperature is sufficient to effect this change. It should be possible to remove the loosely adherent portions with sootblowers or air lances. Water washing should be effective for removing a considerable portion of the corrosive substance from the remanent slag. Prior to firing again, susceptible surfaces should be coated with the oxide material.

## CONCLUSIONS

The following conclusions are derived from the foregoing information together with data presented in reference (a).

Accelerated oxidation of 25-20 chromium-nickel steel surfaces contaminated with vanadium can be reduced substantially by the application of alkaline earth oxides.

Reduced corrosion rates resulting from alkaline earth additions are maintained when there is no further contamination.

Results of the long-term test (165 hours) have indicated that the active contaminant of a corroding slag system is neither consumed nor diluted during the accelerated oxidation of 25-20 chromium-nickel steel.

Certain substances as boric acid, silicon and chromium trioxide intensify the corrosivity of vanadium bearing slags.

Calcium oxide and magnesium oxide additions increase the water solubility of vanadium bearing slags.

Surface Treatments C and D, as described in the report, substantially reduce the accelerated oxidation potential of vanadium bearing slags and scales.

## RECOMMENDATION

It is recommended that consideration be given to trying out the remedial treatments described in this report. The trials should be made by a naval boiler operating agency.

## REFERENCES

- (a) EES Rept 040007BL of 30 Dec 1955
- (b) Morosov, A. N. "Investigation of CaO - V<sub>2</sub>O<sub>5</sub> System," Metallurg, Vol. 13, No. 12, 1938
- (c) Mellor, J. M. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol IX 1933
- (d) EES Rept 040007AP of 15 Dec 1954
- (e) Buckland, B. O. "Modified Residual Fuel for Gas Turbines," ASME Paper No 54-A-246. Dec 1954